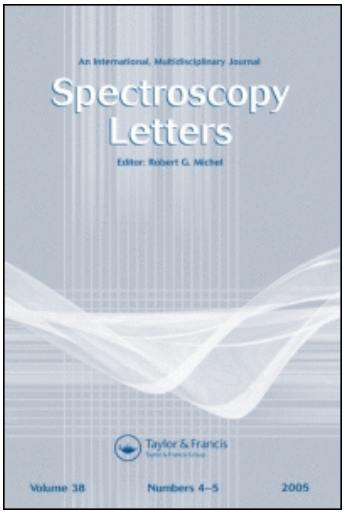

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Scaled DFT Force Constants and Vibrational Spectrum of Cyclopropylamine

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Abstract: The molecular structure and harmonic vibrational frequencies of cyclopropylamine have been calculated using the B3LYP density functional method with the 6-31G(2d,2p) basis set. The scaled DFT force field gives very good reproduction of the experimental vibrational frequencies. Several of the vibrational fundamental modes assigned previously are reassigned on the basis of the B3LYP/6-31G(2d,2p) method and the scaled force field calculations. The optimized scaling factors were used to scale the B3LYP/6-31G(2d,2p) force field of cyclopropane and cyclopropylamine ($-ND_2$) molecules.

Keywords: Cyclopropylamine, density functional theory, molecular structure, normal coordinate analysis, scaled force field

INTRODUCTION

Cyclopropylamine (CPA) is the chemically most reactive cycloalkylamine because of the highly strained bonding in the trimembered ring system, and therefore, it is used as an intermediate for agrochemical active substances. In this respect, the determination of vibrational frequencies from scaled quantum mechanical force field is important in the identification of experimentally observed reactive intermediates for which the theoretically predicted frequencies can serve as fingerprints.

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Concerning the vibrational properties of the CPA molecule, there have been five relevant studies. Kalasinsky et al.[1] presented infrared and Raman spectra of CPA in the gas, liquid, and solid phases and an Ar-matrix infrared spectrum. Compton et al.[2] observed the far-infrared spectrum of CPA and CPA ($-ND_2$) and the mid-infrared ($3200-500\,cm^{-1}$) spectra of the vapor and Raman spectra ($3400-10\,cm^{-1}$) of liquid CPA ($-ND_2$) and proposed tentative assignments based on those of CPA species of Kalasinsky et al.[1] and from cyclopropylhalide.[3] Diello et al.[4] obtained infrared spectra for CPA in the liquid state at room temperature and in the vapor state at a series of temperatures and attempted tentative partial assignment of the fundamental bands. Hamada et al.[5] revised the previously reported vibrational assignments of the fundamental bands of CPA observed between 1300 and $750\,cm^{-1}$. Their assignments were based on the infrared spectra of the normal and N-deuterated species in the gas phase and in Ar-matrix in combination with the existing Raman data and the results of an *ab initio* molecular orbital (MO) calculation. However, there still remain several inconsistencies in the assignment of fundamental vibrations. Hence, we found it necessary to renew the assignment of fundamental vibrations by using an appropriate method. Here we report the B3LYP/6-31G(2d,2p) optimized structure, the assignment of the fundamental vibrations, and the scaled force field of the isolated CPA molecule on the basis of Density Functional Theory (DFT) and normal coordinate calculations. The reason for selecting this computational scheme is that the B3LYP/6-31G method reproduces experimental frequencies with high accuracy if the calculated force field parameters are scaled. The force field scaling procedure compensates for the approximations involved in the DFT calculations and for the anharmonicity that is omitted in the usual harmonic approximation.[6–15]

CALCULATIONS

In the first step, the conformation of CPA was determined. In the second step, optimization and frequency calculations were performed, and in the third step the calculated DFT force field was scaled.

Conformation searching was performed using MM3 molecular mechanics method available in CAChe 5.04 program.[16] In order to determine the most stable conformation, NH_2 group was rotated around the C–N bond between -180° to $+180^\circ$ in 36 steps. The most stable configuration found is shown in Fig. 1. This result is consistent with those given by others (see below).

The molecular structure in the most stable conformation was optimized (refined) at the level of B3LYP functional with the 6-31G(2d,2p) basis set. Same method was used for the frequency calculations. Both optimization and vibrational calculations were carried out using Gaussian 98 program.[17] The input data for the Gaussian 98 were set up using the graphical molecular modelling program GaussView 3.09.[17]

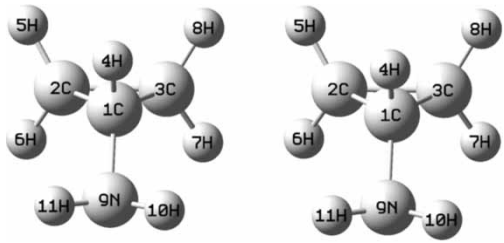

Figure 1. The structure of CPA molecule (stereo view).

The scaling of the DFT force field (complete GVFF) and the calculation of the PED (potential energy distribution) were carried out by using REDONG[18] [which has been adapted to Gaussian 98 program by Professor S. Y. Lee, Department of Industrial Chemistry, Kyungpook National University, Taegu, S. Korea; and modified by one of us (H.Ö.) for restricting the scaling factor system to twenty items], a program for force field calculations written by A. Allouche.[19] The scaling procedure used in the Redong program [described briefly by Lee[14]) is somewhat similar to the modified SQM (scaled quantum mechanical) procedure described in detail by Baker et al.[8] The only significant difference between the original SQM procedure[6] and the modified one employed in this study is that the former uses a nonredundant set of natural internal coordinates and the latter uses a full set of redundant valence coordinates (all possible stretches, all planar bends, all out-of-plane bends, and all proper torsions; for instance, the number of redundant coordinates are 7 for formaldehyde, 20 for ethane, and 33 for CPA). The advantages of redundant coordinates are given by Califano[20] and Baker et al.[8] Following Baker et al., the use of a full set of redundant coordinates opens up the possibility for the direct scaling of individual primitive valence coordinate. This has immediate advantages in terms of ease of use, as no natural internals need to be generated (which may fail for complicated molecular topologies) and simplifies the classification and presorting of the coordinates. In the procedure used in this work, the Cartesian force constants (calculated by Gaussian 98 program) are transformed to a set of force constants in redundant internal coordinates. The calculated vibrational fundamental frequencies are fitted to the experimental ones by direct scaling of the $F = [F_{ij}]$ matrix:

$$F_{ij}^{\text{Scal}} = \sqrt{s_i s_j F_{ij}} \tag{1}$$

The s_i and s_j coefficients (scaling factors) are optimized by the minimization of the quantity χ^2,

$$\chi^2(s) = \sum_{i=1}^{\text{NFRQ}} \left(\frac{\nu_i^{\text{scaled}}(s) - \nu_i^{\text{exp}}}{\nu_i^{\text{exp}}} \right)^2 w_i \tag{2}$$

where NFRQ is the total number of observed frequencies and w_i is the weighting factor for the *i*th fundamental, one or zero (the frequencies that are unobserved or uncertain or considered to have large error bars are assigned to zero weight). In this procedure, PED (potential energy distributions) are also obtained as by-product.

RESULTS AND DISCUSSION

There are several experimental and theoretical works devoted to the structure of CPA. Iijima et al.[21] have determined the structural parameters of CPA molecule by gas-phase electron diffraction at room temperature and also by a combined analysis of data from electron diffraction and microwave literature.[22–25] The crystal structure of cyclopropylamine has been determined by means of x-ray diffraction.[26] *Ab initio* calculations have also been performed to describe the structure of CPA molecule.[27–29] All these studies indicate that the most stable conformation of the CPA molecule is the one in which the NH_2 group is *trans* (in other words, the lone-pair electrons of nitrogen are *cis*) to the plane of the CPA ring (Fig. 1). The structural parameters obtained in this study are presented in Table 1, together with the relevant experimental data for comparison. As seen from Table 1, our optimized bond lengths and angles are in good agreement with the microwave structural results,[25] which are the only experimental results directly comparable to the optimized ground state structure [this is due to the fact that microwave spectroscopy may produce anything from an equilibrium distance, while electron diffraction method may produce a vibrationaly averaged distance and x-ray diffraction measures the distance between centroids of electron density[30]). In other words, spectroscopic methods constitute the most fundamental experimental approaches to molecular structure, as they look to the appropriate wavefunction that contains full knowledge one needs to understand a molecular structure. Therefore, the agreement between the calculated parameters and the microwave structural results indicate the adequacy of the B3LYP/6-31G(2d,2p) procedure used in this work. Table 1 shows that there are considerable differences between our results and the results obtained from x-ray diffraction study. These differences are likely due to the intermolecular interactions such as hydrogen bonding in the solid phase. Another notable is that C1–C2 (C1–C3) bond is shorter than the distal C2–C3 bond. These features may be interpreted as follows: on substitution of NH_2 (acceptor group), the vicinal bonds of the cyclopropyl ring should shorten and the distal bond should lengthen due to the consecutive inductive effects.[31,32] An alternative interpretation based on an orbital interaction picture of the effect of σ acceptor (NH_2) has been given by Clark et al.[33]

Before embarking upon the scaling of the DFT force field and the assignments of the fundamental bands, a few quotable notes about the grouping of

Table 1. Comparison of optimized and experimental geometrical parameters for *trans*-cyclopropylamine (in angstroms for bond lengths and degrees for bond and torsion angles)

Parameter	B3LYP/6-31G(2d,2p)	Microwave[a]	Electron diffraction[b]	Combined analysis[b]	Crystal[c]
C1–C2	1.5066	1.499(0.008)[d]		1.512(3)	1.490(3)
C1–C3	1.5066	1.499(0.008)	1.514(3)	1.512(3)	1.487(3)
C2–C3	1.5108	1.515(0.003)	1.519(3)	1.515(4)	1.492(3)
C1–N9	1.4431	1.452(0.007)	1.429(8)	1.427(8)	1.446(2)
C1–H4	1.0914		1.104	1.093(10)	0.98(3)
C2–H5	1.0835		1.099	1.085(2)	0.092(3)
C2–H6	1.0831		1.099	1.085(2)	1.01(2)
C3–H7	1.0831		1.099	1.085(2)	0.93(2)
C3–H8	1.0835		1.099	1.085(2)	0.98(2)
N9–H10	1.0163	1.026(0.007)	1.031	1.004(20)	0.95(2)
N9–H11	1.0163		1.031	1.004(20)	0.92(2)
C2–C1–C3	60.1855	60.6(0.2)			60.1(1)
C2–C1–N9	116.7957	116.1(0.4)	117.2(6)	116.5(10)	117.5(2)
C3–C1–N9	116.7957		117.2(6)	116.5(10)	118.3(1)
C2–C1–H4	115.7440				118.1(10)
C3–C1–H4	115.7440				115.0(11)
N9–C1–H4	118.4644			117.8(50)	116.2(9)
C1–C2–H5	118.4387				114.8(10)
C1–C2–H6	116.3860				115.7(13)
C3–C2–H5	118.6794				118.1(13)
C3–C2–H6	117.0752				115.8(17)
C2–C3–H7	117.0752				114.6(21)
C2–C3–H8	118.6794				119.0(19)
C1–C3–H7	116.3860				114.9(10)
C1–C3–H8	118.4387				118.0(17)
H5–C2–H6	115.2318		114.5	114.5(9)	118.9(17)
H7–C3–H8	115.2318		114.5	114.5(9)	117.6(21)
C1–N9–H10	110.1205	108.3(0.8)	111.5	117.1(30)	108.8(9)
C1–N9–H11	110.1205		111.5	117.1(30)	108.5(11)
H10–N9–H11	106.3029	105.4(0.7)	106.0	106.0(10)	110.3(15)
H4–C1–C2–H5	−2.2505				
H4–C1–C2–H6	−146.33				
N9–C1–C2–H5	144.5034				
N9–C1–C2–H6	0.4239				
H4–C1–C3–H7	146.33				
H4–C1–C3–H8	2.2505				
N9–C1–C3–H7	−0.4239				
N9–C1–C3–H8	−144.5034				
C2–C1–N9–H10	155.7196				
C2–C1–N9–H11	−87.3693				

(continued)

Table 1. Continued

Parameter	B3LYP/6-31G(2d,2p)	Microwave[a]	Electron diffraction[b]	Combined analysis[b]	Crystal[c]
C3–C1–N9–H10	87.3693				
C3–C1–N9–H11	−155.7197				
H4–C1–C9–H10	−58.4556				
H4–C1–C9–H11	58.4555				
H5–C2–C3–H7	−145.6208				
H5–C2–C3–H8	0.0				
H6–C2–C3–H7	0.0				
H6–C2–C3–H8	145.6208				

[a]From Ref. 25.
[b]From Ref. 21.
[c]From Ref. 26.
[d]Experimental errors are given in parenthesis.

the primitive valance internal coordinates into the plausible sets, each with its own scaling factor, seem to be order. Pulay and his co-workers recommended 12 and 11 common scaling groups for SQM[6] and modified (or primitive) SQM force field procedures, respectively. However, for a molecule with distinct topology of charge density, the number of grouping can obviously be extended. For instance, Baker et al.[8] increased the scaling factors from 3 (recommended) to 11 (at the expense of their transferabilities) for carbonyl-diisocyanate, $(OCN)_2CO$, molecule, scaling separately the C═O (carbonyl), C═O (cyanate), C–N and C═N stretches, the O═C–N, N═C═O, N–C–N and C–N═C bonds, and the O═C–N–C, C═N–C═C and C═N–C–N torsions. (This separation is due to the differences in the topology of electron density; in other words, due to the differences in electron correlation effects at different sites). Besides, it should be noted that in general, the number of scaling groups should be chosen so that the observed frequencies are reproduced reasonably well. Too few scaling groups usually do not give a good fit. On the other hand, if too many groups are chosen, the fit is close to an ordinary spectroscopic force field calculation and the advantages of the *ab initio* calculation are lost.[15]

As to the CPA molecule, the withdrawal of charge from C1 makes that atom more electronegative. The effect of withdrawing charge from C1 atom is in this respect analogous to replacing a more electronegative heteroatom at that side.[32] In this context, we report the Mulliken atomic charges and the bond orders calculated at the B3LYP/6-31G(2d,2p) level: atomic charges (in a.u.): C1 (0.089); C2, C3 (−0.156); H4 (0.041); H5, H6, H7, H8 (0.069); N9 (−0.411); H10, H11 (0.158). Bond orders: C1–C2, C1–C3 (0.60); C2–C3 (1.01); C1–N9 (0.22); C2–H5, C2–H6, C3–H7, C3–H8 (0.99); N9–H10, N9–H11 (0.99). Regarding C1 as a heteroatom, the 33 redundant coordinates of CPA are sorted into 9 scaling groups (the internal

coordinates that are similar in a chemical sense are scaled jointly) according to the recommendation of Baker et al.[7] The scaling factors of these groups and the consequent force constant values were adjusted so as to decrease the differences between the calculated and experimentally observed frequencies. The internal coordinates and the corresponding refined (optimized) scale factors are following: (C1–N9, C1–C3, C1–C2, C2–C3) = 0.9144, (C1–H4) = 0.9445, (C2–H5, C2–H6, C3–H7, C3–H8) = 0.9293, (N9–H10, N9–H11) = 0.9246, (H5–C2–H6, H7–C3–H8 = 0.9528, (H10–N9–H1 = 0.9412, (C1–C2–H5, C1–C2–H6, C1–C3–H7, C1–C3–H8, C2–C3–H7, C2–C3–H8, C3–C2–H5, C3–C2–H6, C2–C1–H4, C3–C1–H4, N9–C1–H4, C1–N9–H1, C1–N9–H11) = 0.9500, (C1–C2–C3, C1–C3–C2, C3–C1–C2, C2–C1–N9, C3–C1–N9) = 1.0322, TORSION (C1–N9) = 0.8331.

As seen in Table 2, over all agreement between the calculated and experimental frequency values are very good. Our average percentage error, over all 27 fundamentals, is 0.47, and RMS (root-mean-square) and mean deviations are 10.23 cm^{-1} and 5.32 cm^{-1}, respectively. On the other hand, excluding the large error bar of ν_{13} vibration, the percentage error, RMS, and mean deviation are 0.28, 7.29, and 4.02, respectively. The corresponding respective RMS values in prefingerprint region ($<500\,cm^{-1}$), fingerprint region ($500–2500\,cm^{-1}$) and postfingerprint region ($>500\,cm^{-1}$) are 0.25, 7.92, and 7.33, respectively. These results are remarkably well compared with the RMS error values presented for 663 vibrational frequencies of 30 organic molecules [7] as follows: RMS: 12.0 (for prefingerprint region, 10.94; fingerprint region, 11.21; and postfingerprint region, 14.92). For some fundamentals (Table 2) the differences between calculated and experimental frequency values are relatively large. These differences are probably due to both genuine experimental error, and more importantly, errors in the harmonic treatment of the floppy vibrations.

The treated experimental wave numbers of CPA in vapour phase are given in Table 2, along with the calculated fundamental frequencies, the potential energy distribution (PED), and the relevant spectral data for comparison. The assignments are based on the PED and the vibrational animations of the fundamental modes.

As for the band assignment in Table 2, the seven fundamental frequencies out of twenty seven presented in the work of Hamada et al.[5] have been revised and reassigned:

(i) Hamada et al.[5] assigned the band at 1173 cm^{-1} to the αCH rocking mode. However, the frequency of αCH rocking vibration is calculated as 1134 cm^{-1} (uncorrected DFT). Therefore, the corresponding experimental band should be observed at a frequency lower than the value of 1134 cm^{-1} due to the floppy (anharmonic) character of the αCH rocking (out of plane bending) vibration. The observed band at 1173 cm^{-1} is assigned to CN stretching vibration according to the present PED

Table 2. Fundamental vibrations of *trans*-cyclopopylamine, $C_3\ H_5\ NH_2$ (in cm^{-1}): comparison between the experimental data, NCA, and DFT results

				Intensity		
Assignment	Obs. (gas)[a,b]	NCA	DFT	Infrared	Raman	PED (%)[c] (>5% taken)
A′						
ν_1 NH_2 s-str.	3,350	3348.38	3481.72	2.2292	155.663	R6 (50), R7 (50)
ν_2 CH_2 a-str.	3,102	3101.49	3235.67	19.5798	28.2758	R8 (23), R9 (23), R10 (27), R11 (27)
ν_3 CH_2 s-str.	3,035	3024.60	3141.47	7.4147	186.477	R8 (27), R9 (27), R10 (23), R11 (23)
ν_4 CH* str.	2,975	2974.99	3061.39	54.6717	99.6486	R5 (99)
ν_5 NH_2 sci.	1,618	1617.99	1665.41	9.6566	11.2443	A1 (67), A15 (16), A16 (16)
ν_6 CH_2 sci.	1,457	1474.73	1508.82	13.4683	7.7537	A2 (13), A3 (13), A4 (6), A5 (6), A6 (5), A7 (5), A8 (7), A9 (7)
ν_7 CH* bend.	1,375	1376.69	1414.73	22.1900	6.9984	R1 (13), A12 (21), A13 (20), A14 (17)
ν_8 CH bend.	1,234	1233.99	1242.66	0.4775	19.487	R1 (12), R2 (8), R3 (12), R4 (12), A12 (16), A13 (16), A14 (8)
ν_9 CN str.	1,173	1162.66	1178.90	7.8175	5.3253	R1 (26), A8(12), A9 (13), A10 (9), A11(11), A14 (8), A17 (6), A18 (6)
ν_{10} CH_2 wag.	1,020	1028.73	1055.49	12.1943	2.1819	R2 (15), A4 (9), A5 (7), A6 (9), A7 (7), A9 (6), A10 (12), A11 (16)
ν_{11} CN str.	989	989.00	1018.65	6.2352	10.923	R1 (26), R2 (17), A1 (5), A6 (5), A8 (9), A9 (11), A15 (6), A16 (6)
ν_{12} NH_2 wag.	832	829.71	863.71	111.53	3.3895	R1 (18), A1 (15), A15 (18), A16 (20)
ν_{13} C-C str.	763	765.43	818.37	21.4693	5.5412	R2 (10), R3 (6), R4 (5), A4 (9), A5 (9), A6 (9), A7 (8), A15 (5), A16 (6), A20 (6)
ν_{13} CH_2 rock.	749	742.44	769.65	2.7572	5.0378	A4 (22), A5 (20), A6 (20), A7 (18)

ν_{15} CCN bend. A″	408	408.00	408.33	5.5639	1.1274	A12 (8), A13 (8), A17 (33), A18 (32)
ν_{16} NH_2 a-str.	3,414	3423.48	3555.28	0.0079	83.887	R6 (50), R7 50)
ν_{17} CH_2 a-str.	3,089[d]	3115.05	3221.95	0.1818	84.278	R8 (22), R9 (22), R10 (28), R11 (28)
ν_{18} CH_2 s-str.	3,023	3019.38	3135.78	23.4260	23.565	R8 (28), R9 (28), R10 (22), R11 (22)
ν_{19} CH_2 sci.	1,424	1423.16	1459.73	0.7856	7.7846	A2 (18), A3 (18), A4 (8), A5 (9), A6 (8), A7 (7), A8 (7), A9 (7), A10 (7), A11 (7)
ν_{20} NH_2 twist.	1,288	1287.97	1282.91	0.9922	1.5536	A15 (43), A16 (44)
ν_{21} CH_2 twist.	1,213	1213.00	1199.97	0.0661	7.2563	A4 (22), A5 (20), A6 (23), A7 (20)
ν_{22} CH rock.	1,149	1149.00	1134.11	0.3122	1.1236	A10 (8), A11 (10), A12 (27), A13 (36)
ν_{23} CH_2 wag.	1,045	1044.98	1070.16	0.8438	0.1727	A4 (13), A5 (10), A6 (14), A7 (9), A8 (13), A9 (17), A10 (7), A11 (10)
ν_{24} CCC astr.	884	884.07	898.59	7.2470	9.3035	R3 (17), R4 (19), A8 (6), A9 (7), A15 (6), A16 (6), A19 (8), A20 (8)
ν_{25} CH_2 rock.	821	823.32	839.27	2.4311	4.4885	A8 (13), A9 (14), A10 (17), A11 (20), A12 (5), A13 (6)
ν_{26} CN bend	396	396.00	396.37	6.0838	0.2603	A8 (9), A9 (9), A10 (6), A11 (6), A17 (26), A18 (20), T (6)
ν_{27} C–N tor.	250	250.00	270.75	29.720	1.6486	A15 (7), A16 (5), A (6), T (75)

str., stretching; sci., scissoring; bend., bending; a, symmetric; s, symmetric; tor., torsion; Obs., observed; PED, Potential Energy Distribution; NCA, Normal Coordinate Analysis; DFT, Density Functional Theory.

[a]Taken from Ref. 5.

[b]Reassigned wavenumbers are underlined.

[c]R1: C1–N9, R2: C2–C3, R3: C1–C3, R4: C2–C1, R5: C1–H4, R6: N9–H10, R7: N9–H11, R8: C2–H5, R9: C3–H8, R10: C2–H6, R11: C3–H7, A1: H10–N9–H1, A2: H5–C2–H6, A3: H7–C3–H8, A4: C3–C2–H5, A5: C2–C3–H8, A6: C3–C2–H6, A7: C2–C3–H7, A8: C1–C2–H6, A9: C1–C3–H7, A10: C1–C2–H5, A11: C1–C3–H8, A12: C3–C1–H4, A13: C2–C1–H4, A14: N9–C1–H4, A15: C1–N9–H1, A16: C1–N9–H1, A17: C2–C1–N9, A18: C3–C1–N9, A19: C1–C2–C3, A20: C2–C3–C1, A21: C3–C1–C2, T: torsion (C1–N9).

[d]Estimated as ν_{17} (estimated) = ν_2 (obs.) × ν_{17} (DFT)/ν_2 (DFT).

animation calculations. Kalasinsky et al.[1] observed a band at 1105 cm^{-1} in the gas phase infrared spectrum of CPA (and assigned it to CH_2 twisting vibration). This band has also been observed by Hamada et al.[5] but they have not regarded it as a fundamental. We have estimated frequency of αCH rocking vibration as 1103 cm^{-1} from the equation $\nu_{12}(\text{estimated}) - \nu_{23}(\text{observed}) \times \nu_{12}(\text{DFT})/\nu_{23}(\text{DFT})$ [PED calculations indicate that the same internal coordinates are dominantly participated in ν_{12} and ν_{23} modes (Table 2)]. In addition, Raman spectrum of liquid CPA from Aldrich Spectral Library shows a weak band at ca. 1100 cm^{-1}. Therefore, the gas phase infrared band at 1105 cm^{-1} has been regarded as a fundamental and assigned to αCH rocking vibration (Table 2).

(ii) Hamada et al.[5] have observed a weak (gas phase) infrared band at 1288 cm^{-1} and assigned to the NH2 twisting vibration. However, the gas phase spectrum of CPA from NIST Chemistry WebBook shows that this very weak band seems not to be discriminated from the background signals. On the other hand, the DFT calculations (PED and animation of the modes) show that the NH_2 twisting vibration is at 1283 cm^{-1} (uncorrected DFT value) suggesting that the floppy NH_2 twisting vibration should be lower than the value of 1283 cm^{-1}. Therefore, the band at 1288 cm^{-1} has been disregarded as a fundamental of CPA in this study; and the band at 1234 cm^{-1} has been assigned to NH_2 twisting vibration (Table 2).

(iii) Hamada et al.[5] and Kalasinsky et al.[1] estimated the CH_2 antisymmetric stretching vibration as 3075 and 3100 cm^{-1}, respectively. This fundamental has been assigned to zero weight in the scaled DFT force field calculation.

(iv) Hamada et al.[5] assigned the band at 832 cm^{-1} to the CCC asymmetric stretching vibration. However, the PED and the vibrational animation indicate that the DFT frequency of this band is calculated as 899 cm^{-1} and its corrected value is 884 cm^{-1}. The corresponding observed band frequency should be close to this value due to the low anharmonic character of this vibration. Accordingly, the experimental band at 884 cm^{-1} has been assigned to the CCC antisymmetric streching vibration. This assignment is consistent with that of Kalasinsky et al.[1]

(v) The band observed at 832 cm^{-1} has been assigned to the NH_2 waging vibration, which has been calculated as 864 cm^{-1} and its refined value is 839 cm^{-1} (Table 2).

(vi) Hamada et al.[5] and Kalasinsky et al.[1] assigned the band at 763 cm^{-1} to NH_2 waging and CH_2 rocking, respectively. As seen from corresponding PED calculation in Table 2, this fundamental mode is the mixture of NH2 waging, CH2 rocking, and CCC antisymmetric stretching vibrations (in other words, the vibration is mainly delocalized over the C–C–H, C–N–H, C–C1–C, H–N–H and C–C coordinates).

For this reason, this vibration has been named "NH_2, CH_2, CCC deformations."

(vii) The experimental band given at 749 cm^{-1} (Table 2) has been assigned to ring deformation by Hamada et al.,[5] but the current calculations indicate that this band should be assigned to CH_2 rocking vibration. It should be noted that our other 20 band assignments are well consistent with those of Hamada et al.[5] The seven inconsistent assignments are possibly due to the fact that the assignments by Hamada et al.[5] are based on the PED calculated using HONDO and Gaussian 80 programs at HF/4-31G(N*) level, while the current assignments are based on PED results calculated at a higher level of theory; and in addition, the vibrational animations of the reassigned fundamentals displayed using GaussView 3.09 graphics program are not consistent with the PED calculations of Hamada et al.,[5] but consistent with the current ones.

Table 3. Fundamental vibrations of cyclopropane: comparison between the experimental and the theoretical data obtained using scale factor transferring (SFT) and least squares scaling (LSS) methods

Assignment[a]	Observed (gas)[a]	SFT	LSS	DFT
CH_2 rocking, E′	739	717	720	736
	739	717	720	736
CH_2 rocking, A_2'	854	835	839	857
CH_2 wagging, E′	868	879	868	889
	868	879	868	889
Ring deformation, E′	1,028	1,031	1,033	1,057
	1,028	1,031	1,031	1,057
CH_2 wagging, A_2'	1,070	1,054	1,057	1,081
CH_2 twisting, A_1''	1,126	1,127	1,130	1,156
Ring breathing, A_1'	1,188	1,170	1,188	1,215
CH_2 twisting, E′	1,188	1,185	1,188	1,215
	1,188	1,185	1,188	1,221
CH_2 deformation, E′	1,438	1,442	143	1,479
	1,438	1,442	1,438	1,479
CH stretching, A_1'	1,479	1,484	1,483	1,525
CH stretching, E′	3,024	3,021	3,018	3,133
	3,024	3,021	3,018	3,133
CH stretching, A_1'	3,038	3,029	3,026	3,142
CH stretching, E′	3,082	3,096	3,092	3,211
	3,082	3,096	3,092	3,211
CC stretching, A_2''	3,102	3,117	3,114	3,233

[a]Taken from Ref. 34.

Table 4. Fundamental vibrations of cyclopropylamine-ND_2 (C3H5ND2): comparison between the experimental and the theoretical data obtained using scale factor transferring (SFT) and least squares scaling (LSS) methods

Assignment	IR (gas)[a]	Raman (gas)[a]	SFT	LSS[b]	DFT
ν_{27} ND_2 torsion	188		186	188	203
ν_{26} CN out-of-plane bend		(380 liquid)	371	370	369
ν_{15} CN in plane bend	390	391	391	390	392
ν_{13} ND_2 wag.	617	618	659	655	674
ν_{23} CH_2 twist.	677	678	747	742	766
ν_{14} CH_2 rock.	752	755	785	775	804
ν_{25} CH_2 rock.	810	812	803	810	825
ν_{24} ring def.	835		832	835	846
ν_{12} ring def., CN str.	969	970	964	975	992
ν_{11} CH_2 wag.	1,018	1,021	1,027	1,019	1,053
ν_{22} ND_2 twist.	1,026		1,043	1,030	1,063
ν_{21} CH_2 wag.	1,049		1,048	1,035	1,072
ν_9 αCH out-of-plane bend.	1,107	1,108	1,049	1,113	1,143
ν_{10} CH_2 rock, NH_2 twist.		1,158	1,116	1,156	1,144
ν_{20} CH_2 twist.	1,180		1,171	1,220	1,200
ν_8 ring breathing	1,219		1,192	1,224	1,239
ν_5 ND_2 deformation	1,242		1,225	1,249	1,263
ν_7 CH in-plane bend	1,376		1,368	1,378	1,409
ν_{19} CH_2 deformation		(1,420 liquid)	1,368	1,422	1,461
ν_6 CH_2 deformation	1,460		1,458	1,470	1,509
ν_1 ND_2 symmetric stretch		2,436	2,426	2,429	2,517
ν_{16} ND_2 antisymmetric stretch	2,550		2,426	2,532	2,619
ν_4 αCH stretch	2,972	2,974	2,975	2,975	3,062
ν_{18} CH_2 symmetric stretch	3,021	3,018	3,015	3,021	3,136
ν_3 CH_2 symmetric stretch		3,031	3,022	3,026	3,142
ν_{17} CH_2 antisymmetric stretch		3,087	3,101	3,103	3,222
ν_2 CH_2 antisymmetric stretch	3,100		3,114	3,117	3,236

[a]Taken from Ref. 2.

[b]Calculations are based on infrared wavenumbers (the Raman wavenumbers are used for LSS where infrared wavenumbers are not available).

It is of interest to apply the scale factors derived from cyclopropylamine to cyclopropane and CPA ($-ND_2$) molecules.

Cyclopropane: We optimized and calculated the force constants of cyclopropane using B3LYP/6-31G (2d,2p) procedure. The force constants are divided into five groups as follows: C–C stretchings, C–H stretchings, C–C–C bendings, H–C–H bendings, and C–C–H bendings. Corresponding respective scale factors derived from scaling of CPA are these: C–C, 0.9144; C–H, 0.9293; C–C–C, 1.0322; H–C–H, 0.9428; and C–C–H, 0.9500. For the purposes of comparison and discussion, the least square scaling of B3LYP/6-31G(2d,2p) force field procedure for cyclopropane has also been performed (Table 3). The calculated and experimental vibrational frequencies[33] of cyclopropane are compared in Table 3. The average percentage, main deviation and RMS errors are 0.84, 9.71, and 11.82, respectively. These error values are well compared with the criteria values stated above.

Cyclopropylamine ($-ND_2$): In this case, the computation is also performed using the B3LYP/6-31G(2d,2p) force field and the optimized scale factors for CPA molecule. In addition, for the purpose of comparison, least squares scaling force field calculations have also been performed on this molecule. For these calculations, $\nu_{22} = 1026\,cm^{-1}$ frequency of CPA molecule from Table 2 has been used, as this fundamental is missing in Ref. 2. The calculated and experimental[2] frequencies of CPA ($-ND_2$) are given in Table 4. The assignments are based on the vibrational animations of CPA (–ND2) (3 out of 27 has been reassigned). The average percentage, main deviation, and RMS values are 3.88, 14.95, and 21.66, respectively. These error values may be appraised as "very poor". These disappointing results are possibly due to both the anharmonicity differences between NH_2 and ND_2 groups, and, more importantly, the genuine experimental errors. Similar differences are also observed between the experimental wavenumbers and the wavenumbers obtained from the least squares scaling DFT force field calculation performed on cyclopropylamine ($-ND_2$) as done for cyclopropylamine (Table 4).

The conclusion to be drawn from the above discussion is that B3LYP/6-31G(2d,2p) and least squares scaling force field procedures are adequate to predict the general valance force field (GVFF) and the resultant vibrational spectrum of CPA molecule.

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